Direct Methanol Fuel Cell with Polyphosphazene Membrane

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INTRODUCTION

Prof. Pintauro at Tulane University has been developing procedures to fabricate ion exchange membranes from sulfonated/crosslinked phosphazene polymers. The following are the principal characteristics of such membranes:

(i) The methanol diffusivity in this membrane is almost an order of magnitude lower than that in Nafion 117.

(ii) The stability of these membranes is as good as Nafion (in short term tests), and the mechanical properties of PVDF blended membranes are adequate to make membrane electrode assemblies.

(iii) Proton conductivity of these films (when properly equilibrated with water) is about 25-50% that of Nafion 117. At the lower current density of operation of portable DMFC, this lower conductivity value only slightly reduces the performance. Further development of the membrane may result in conductivity improvement.

EXPERIMENTAL

Membranes were prepared, characterized and supplied by Prof. Pintauro's group at Tulane University, New Orleans. Membrane variations included type and extent of cross-linking, ion exchange capacity and the % of inert polymeric filler additive.

Membranes were characterized for their methanol diffusivity, conductivity, performance in DMFC, including the extent of cross-over. A standard H-Cell arrangement was used to determine the diffusion coefficient of methanol through the polymer electrolyte membranes. 1M methanol was placed on one side of the H-cell and water on the other side. Magnetic stirrers were used to vigorously stir both sides to ensure uniform mixing.

Methanol analysis was done using a Shimadzu GC-14A with a J&W DB-WAX capillary column and an FID detector. Liquid samples of 0.5µL were taken using a 0.5microliter syringe. The injector temperature was set at 250°C and the detector temperature was set at 300°C. The initial column temperature was set at 35°C. After 5 min, the temperature was ramped at 10°C/min to 110°C, which was maintained for another 2 minutes. Peak area was converted to methanol concentration using data from a previous calibration experiment.

A four-probe conductivity cell was used to measure the in-plane conductivity of the ionomeric membranes.

Membrane performance was assessed in standard fuel cell hardware. Methanol cross-over was assessed by measuring the CO_2 content in the cathode exhaust using a Vysala IR detector.

RESULTS AND DISCUSSION

These SPOP membranes exhibited room temperature conductivities in the range of 0.02 - 0.07 S/cm. The methanol diffusion coefficients of these membranes are in the range 3 x 10^{-7} - 5 x 10^{-8} cm^2/s and compare favorably with the diffusion coefficient of 2 x 10^{-6} cm^2/s observed with Nafion 117. Cyclic voltammetric scans indicate that the membrane is inert (i.e., no redox activity) in the potential range 0 - 1.2 V (vs. RHE).

Some of the early fuel cells that we tested with the phosphazene membrane gave inferior DMFC performance in our tests. Therefore, in view of the property of Nafion to form a good membrane electrode interface, and the property of polyphosphazene to decrease methanol permeation, Nafion and polyphosphazene were combined into a single MEA. As a first embodiment, we prepared separate anode and cathode membrane assemblies by bonding them individually to Nafion 112 (to keep resistance to minimum). We then made a sandwich of polyphosphazene (#2031) with the Nafion bonded electrodes, lightly hot pressed the assembly and tested it in a DMFC. The performance results of this Pt/Ru|Nafion 112|phosphazene|Nafion112|Pt black assembly are compared in **Figure 1** to a membrane electrode assembly prepared with only a phosphazene membrane. The difference in performance between the direct bonded and sandwiched assemblies is relatively small with this particular membrane. We believe that the softness of this membrane led to a good interfacial bond between membrane and electrodes. The good interface together with the better conductivity of this membrane are probably responsible for this superior performance.

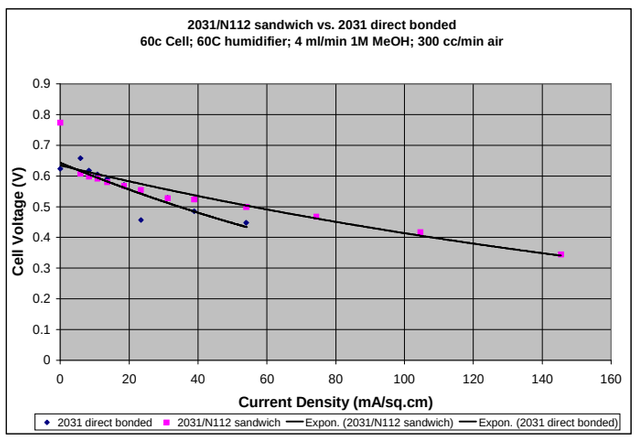

Figure 1. Performance comparison of SPOP membrane # 2031 in direct bonded and sandwich configurations in DMFC. Electrode area: 3.24 cm^2, 1 M methanol, 4ml/min flow rate, air: 300 cc/min.

Fuel efficiency estimated by measuring CO_2 at the cathode showed at least 30% improvement over Nafion in the current density range of 50-100 mA/cm^2.

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